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File: USPT

Jan 28, 1997

DOCUMENT-IDENTIFIER: US 5597780 A

TITLE: Low volatility formulations of microencapsulated clomazone

Abstract Text (1):

An herbicidal composition containing from 1 to 4 pounds of clomazone per gallon of formulation and having a clomazone volatility less than fifty percent of that of an emulsifiable concentrate containing four pounds of clomazone per gallon of formulation is prepared by the interfacial reaction of polymethylene polyphenyl isocyanate with a polyfunctional amine selected from ethylenediamine, diethylenetriamine, triethylenetetramine, 1,6-hexanediamine, and their mixtures in an aqueous phase optionally containing from 0.05 to 0.25 weight percent of a xanthan gum viscosity modified/stabilizer. Several such formulations and the method of their preparation are described.

US Patent No. (1):5597780Brief Summary Text (6):

The process of the invention involves the following steps: (a) providing an aqueous phase containing an emulsifier, preferably a partially hydrolyzed polyvinyl alcohol; an antifoam agent, and optionally a xanthan gum viscosity modifier/stabilizer; (b) providing a water immiscible phase consisting of clomazone and polymethylene polyphenyl isocyanate, with or without a hydrocarbon solvent; (c) emulsifying the water immiscible phase in the aqueous phase to form a dispersion of water-immiscible droplets throughout the aqueous phase; (d) agitating the dispersion while adding to it, either neat or in aqueous solution, ethylenediamine, diethyltriamine, triethylenetetramine, 1,6-hexanediamine, or a mixture of the polyfunctional amines, thus forming a polyurea shell wall around the water-immiscible droplets. Once the microcapsules are formed, the suspension is cured by moderate heating, after which one or more stabilizing agents, such as propylene glycol, xanthan gum, smectite clay, or an ionic dispersing agent such as a sulfonate of an alkyl naphthalene, may be added, as is well-known in the art. It has also been found that adjusting the pH of the formulation from mildly acidic to mildly alkaline conditions, such as a range of from 6.5 to 9.0, e.g., pH 8.9, results in a formulation having improved storage stability. The addition of these materials after encapsulation and curing to adjust viscosity and suspensibility is not seen to have any effect on the loss of clomazone through volatility or on the herbicidal efficacy of the formulation.

Brief Summary Text (7):

The aqueous phase will ordinarily contain 0.3 to 3.0, preferably 0.8 to 2.0, weight percent of one or more emulsifiers, e.g., polyvinyl alcohol, 0.05 to 0.20, preferably 0.06 to 0.15, weight percent of the xanthan gum viscosity modifier/stabilizer, if it is used, and 0.1 to 1.0, preferably 0.4 to 0.9, weight percent of the antifoam agent.

Brief Summary Text (8):

The water-immiscible phase will ordinarily consist of 60 to 85, preferably 65 to 77, weight percent of clomazone, an amount of polymethylene polyphenyl isocyanate (PMPPI) such that the ratio of clomazone to PMPPI is in the range of 1:1 to 6:1, preferably 4.5:1 to 4.8:1, and an aromatic hydrocarbon solvent for the two solutes. However, use of solvent is optional in the preparation of formulations containing more than about two pounds of clomazone per gallon of formulation. In such

preparations a small amount of solvent may still be used to depress the melting point.

Detailed Description Text (5):

In a one-liter stainless steel beaker were placed 20.0 grams of the aqueous 20% polyvinyl alcohol solution prepared above, 1.8 grams of 100 % of a polydimethyl siloxane antifoam agent (Dow Corning.RTM. 1500), 15.0 grams of aqueous 2% xanthan gum (Kelzan.RTM. M), and 400.0 grams of water. After this mixture was mixed for 20 seconds at high speed in a high-shear mixer, a pre-blended solution of 140.0 grams of clomazone, 30.0 grams of polymethylene polyphenyl isocyanate (PMPPI, Mondur.RTM. MR), and 30.0 grams of petroleum solvent (a mixture of C.sub.9 -C.sub.15 aromatic, naphthalene-depleted, hydrocarbons, flash-point 95.degree. C., Aromatic 200 ND) was added, and the mixture was emulsified in the high shear mixer for five minutes. The mixture was then placed in a one-liter jacketed resin flask with the jacket pre-heated to 50.degree. C. The mixture was stirred at a moderate speed with an air-powered stirrer, and a solution of 19.0 grams of triethylenetetramine (TETA) in 35.0 grams of water was added in one portion. The mixture was then stirred at 50.degree. C. for four hours. After this time, 2.5 grams of a smectite clay containing magnesium aluminum silicate, titanium dioxide, and cristobalite (Veegum.RTM. Ultra), and 15.0 grams of aqueous 2% xanthan gum (Kelzan.RTM. M) were added to stabilize the formulation. The formulation was then stirred for about one hour and stored for later use.

Detailed Description Text (9):

A solution of 5.24 pounds of polyvinyl alcohol (Airvol 203), 2.38 pounds of an aqueous solution of 20% polydimethyl siloxane antifoam agent (Dow Corning.RTM. 1520), and 0.21 pound of xanthan gum viscosity modified/stabilizer (Kelzan.RTM. S) in 284.20 pounds of water was placed in a 500 gallon stainless steel vessel, and stirred at 80.degree. C. for one hour. After this time the solution was cooled to 20.degree. C. and placed in an 80 gallon batch homogenizer. With the homogenizer in operation, a pre-blended solution of 161.34 pounds of technical clomazone, 34.75 pounds of polymethylene polyphenyl isocyanate (PMPPI, Mondur.RTM. MR), and 34.75 pounds of petroleum solvent (a mixture of C.sub.9 -C.sub.15 aromatic hydrocarbons, flash-point 95.degree. C., Aromatic 200) was fed by gravity into the homogenizer during a 15 to 90 second period. The mixture was homogenized for two to three minutes. Upon completion of the homogenization, the mixture was placed in a jacketed reactor with the jacket pre-heated to 50.degree. C. To the jacketed reactor was added, over a period of 30 seconds, an amine mixture consisting of 10.97 pounds of triethylenetetramine (TETA) and 10.97 pounds of 1, 6-hexanediamine (HDA). After the amine addition was completed, the mixture was cured with agitation at 25.degree. C. to 50.degree. C. during a four hour period. At the end of the curing period, 35.70 pounds of propylene glycol and 1.19 pounds of xanthan gum were added to stabilize the formulation. The formulation was then cooled to below 30.degree. C. and stored for later use. It had a viscosity of 1870 cps and a suspensibility of 82%. Both formulations described in Tables 3 and 4 were prepared in the manner of Example 2. Formulation A-1 is a larger scale version of Formulation A, and Formulation E-1 is a larger scale version of Formulation E.

Detailed Description Paragraph Table (1):

TABLE 1													Preparation of Clomazone Capsule Suspension (CS) Formulations (Components and Amounts)									
													Formulation Weight (grams) (lb/gal) A (1.5) B									
(2.0) C (1.5) D (2.0) E (2.0) F (2.0)																						
Component Aqueous Solution Water	430.7	493.00	430.70	493.00	493.00	493.00	493.00	PVA	4.0													
4.58 4.00 4.58 4.58 4.58 Xanthan Gum	0.3	0.35	0.30	0.35	0.35	0.35	0.35	(a.i.) Antifoam														
1.8 2.06 1.80 2.06 2.00 2.06 (a.i.) Isocyanate Solution	Clomazone	140.0	280.00																			
140.00 280.00 280.00 280.00 Petroleum	30.0	60.00	30.00	60.00	60.00	60.00	60.00	Solvent														
PMPPI 30.0 60.00 30.00 60.00 60.00 60.00 Amine Solution	TETA	19.0	38.00	--	--	19.00																
9.50 HDA -- -- 19.00 30.00 19.00 28.50 Water	35.0	62.00	31.00	70.00	62.00	62.00	62.00	Post														
Encapsulation Stabilizers Smectite Clay	2.5	in Water	14.7	--	--	--	--	Propylene														
-- 19.60 9.00 18.00 9.00 18.00 Glycol Xanthan	0.3	0.40	1.00	2.00	1.00	2.00	2.00	Gum														
(a.i.)	Weight (grams) Formulation (lb/gal) G																					
(2.0) H (2.0) I (2.0) J (2.0) K (2.0)																						
Component Aqueous Solution Water	493.00	493.00	493.00	493.30	493.00	PVA	4.6	4.6	4.58													
4.58 4.58 Xanthan Gum (a.i.)	0.4	0.4	0.35	--	0.35	Antifoam	(a.i.)	2.1	2.06				2.06	2.06								

PVA Airvol .RTM. 203 polyvinyl alcohol. Xanthan gum Kelzan .RTM. M and Kelzan S xathan gums differ in that S has been surface treated to improve ease of dispersion. M was used in all cases except post encapsulation in Formulations A, C, D, F, and H. Antifoam Dow Corning .RTM. 1500 is 100% polydimethyl siloxane. Dow Corning 1520 is a 20% solution; amount shown is active ingredient (a.i.). 1500 was used in Formulations A and C; 1520 in the others. Petroleum solvent Aromatic 200, a mixture of C.sub.9 -C.sub.15 aromatic hydrocarbons, flash point 95.degree. C. That used in Formulation A was naphthalene depleted. PMPPI Mondur .RTM. MR polymethylene polyphenyl isocyanate. TETA triethylenetetramline. HDA 1,6hexanediamine. Smectite clay Veegum .RTM. Ultra clay consisting of magnesium aluminum silicates with titanium dioxide and cristobalite present. EDA ethylenediamine. DETA diethylenetriamine.

Formulation Percent (wt/wt) (lb/gal) A (1.5)																	
B (2.0)	C (1.5)	D (2.0)	E (2.0)	F (2.0)													
Component	Clomazone	19.77	27.45	20.09	27.45	27.72	27.45	Encapsulating Polymer	PMPPI								
4.24	5.88	4.31	5.88	5.94	5.88	HDA	--	--	2.72	2.94	1.88	2.79	TETA	2.68	3.73	--	--
1.88	0.93	Polyvinyl	0.56	0.45	0.57	0.45	0.45	0.45	Alcohol	Petroleum	4.24	5.88	4.31				
5.88	5.94	5.88	Solvent	Polydimethyl	0.25	0.20	0.26	0.20	0.20	0.20	Siloxane-	Antifoam					
Agent	Xanthan	0.08	0.07	0.19	0.23	0.13	0.23	Gum-	Viscosity Modifier/	Stabilizer							
Propylene	1.92	1.29	1.77	0.89	1.77	Gylcol	Stabilizer	Smectite	0.35	--	--	--	--	--	--	--	
Clay-	Viscosity Modifier	Water	67.83	54.42	66.26	55.20	54.95	54.42	Total	100.00							
100.00	100.00	100.00	100.00	100.00	100.00							Percent					
(wt/wt)	Formulation	(lb/gal)	G (2.0)	H (2.0)	I (2.0)	J (2.0)	K (2.0)										
Component Clomazone 28.00 26.7 27.45 27.45																	
27.45	Encapsulating Polymer	PMPPI	6.00	5.70	5.88	5.88	5.88	EDA	--	--	0.75	0.75	TETA				
--	--	2.98	2.98	DETA	1.12	1.80	--	--	3.73	HDA	1.90	1.80	--	--	Polyvinyl Alcohol		
0.46	0.44	0.45	0.45	0.45	Petroleum	Solvent	6.00	5.70	5.88	5.88	5.88	Polydimethyl					
0.21	0.20	0.20	0.20	0.20	Siloxane-	Antifoam	Agent	Xanthan	Gum-	0.04	0.13	0.07	0.04				
0.07	Viscosity Modifier/	Stabilizer	Propylene	--	4.67	1.92	1.92	1.92	Gylcol								
Stabilizer	Water	56.27	52.86	54.42	54.45	54.42	Total	100.00	100.00	100.00	100.00	100.00					
100.00																	

<u>TABLE 3</u>						<u>Large Scale Preparation of Clomazone</u>							
<u>CS Formulations (Components and Amounts)</u>								<u>Weight (lbs)</u>	<u>Formulation (lb/gal)</u>				
E-1 (2.0)	P (3.0)							<u>Component Aqueous Solution</u>					
Water	222.85	284.20	274.4	PVA	2.000	5.24	5.05	Xanthan Gum	0.300	0.21	0.22	<u>Antifoam</u>	
0.900	2.38	4.30	Isocyanate Solution	Clomazone	70.000	161.34	289.8	Petroleum Solvent					
15.000	34.75	31.2	PMPPPI	15.000	34.75	62.5	Amine Solution	TETA	9.500	10.97	HDA	--	
10.97	DETA	--	--	40.0	Water	17.500	40.50	Post Encapsulation Additives	Propylene Glycol	--	35.70	39.8	
Xanthan Gum	--	1.19	26.2*	Smectite Clay	1.250	--	--	Bactericide					
A.sup.1	0.009	--	--	Bactericide B.sup.2	0.177	--	--	Bactericide C.sup.3	--	--	0.4	Na	
Naphthalene Sulfonate	.sup.4	--	--	5.3 Concentrated Aqueous Hcl	--	--	22.33						
Amphoteric Surfactant	.sup.5	--	--	26.0								.sup.1	
Dowcide .RTM.	A (ophenylphenate tetrahydrate)	.sup.2	Legend .RTM.	MK (mixture of 2methyl-4-isothiazolin-3-ones)	.sup.3	Proxel .RTM.	(1,2benzisothiazolin-3-one)	.sup.4	Sodium salt of sulfonated naphthalene condensate	.sup.5	Mirataine .TM.	H2CHA (sodium lauriminodipropionate) *as a 1.9 wt % dispersion.	

TABLE 4 Large Scale Clomazone CS Formulations													
(Components and Weight/Weight Percents) Percent (wt/wt) Formulation A-1 E-1 P													
Component Clomazone 19.74 25.93 35.02													
Encapsulating Polymer PMPPI	4.23	5.59	7.55	HDA	--	1.76	--	TETA	2.68	1.76	--	DETA	--
-- 4.83 Polyvinyl Alcohol	0.56	0.84	0.61	Petroleum Solvent	4.23	5.59	3.77						

Polydimethyl Siloxane-Antifoam Agent 0.25 0.38 0.53 Xanthan Gum-Viscosity 0.09 0.23
 0.09 Modifier/Stabilizer Propylene Glycol Stabilizer -- 5.74 4.81 Smectite
 Clay-Viscosity Modifier 0.37 -- -- Bactericides 0.05 -- 0.05 Na Naphthalene
 Sulfonate Condensate -- -- 0.65 Concentrated Aqueous Hcl -- -- 2.70 Amphoteric
 Surfactant -- -- 0.94 Water 67.80 52.18 38.45 Total 100.00 100.00 100.0

Detailed Description Paragraph Table (5):

TABLE 5 Unsatisfactory Clomazone CS
 Formulations (Components and Weight/Weight Percents) Percent (Wt/Wt) Formulation L M
 N O Component Clomazone 20.38 30.43 20.38
 27.45 Encapsulating Polymer PMPPI -- -- 4.37 5.88 TDI 4.37 1.73 -- -- TETA 2.77 --
 2.77 DETA -- 0.73 -- 3.73 EDA -- 0.15 -- -- Polyvinyl Alcohol 0.58 2.72 0.58 0.45
 Petroleum Solvent 4.37 -- 4.37 5.88 Polydimethyl Siloxane 0.26 0.28 0.26 0.20
 Antifoam Agent Xanthan Gum Viscosity 0.04 -- -- 0.04 Modifier/Stabilizer Propylene
 Glycol Stabilizer -- -- -- 1.92 Water 67.23* 63.96 67.27* 54.45* Total 100.00 100.00
 100.00 100.00 TDI is toluene diisocyanate
 DETA is diethylenetriamine EDA is ethylenediamine *Ten mL of a 10% solution of
 xanthan gum in propylene glycol was added to stabilize the formulation after it was
 prepared.

CLAIMS:

1. A process for the preparation of herbicidally effective formulations of clomazone having a volatility less than fifty percent of the volatility of an emulsifiable concentrate of clomazone containing four pounds of clomazone per gallon of formulation which comprises microencapsulating the clomazone by interfacial polymerization by the steps of:

- a) providing an aqueous phase containing 0.3 to 3.0 wt. % of one or more emulsifiers; optionally 0.02 to 0.20 wt. % of a xanthan gum viscosity modifier/stabilizer, and 0.1 to 1.0 wt. % of an antifoam agent;
- b) providing a water immiscible phase consisting of clomazone, polymethylene polyphenyl isocyanate (PMPPI), and a hydrocarbon solvent; the weight ratio of clomazone to PMPPI being in the range of 1:1 to 6:1;
- c) emulsifying the water immiscible phase in the aqueous phase, forming a dispersion of water immiscible droplets throughout the aqueous phase;
- d) agitating the dispersion while adding thereto an aqueous solution of 15 to 100 weight percent of at least one polyfunctional amine selected from ethylenediamine (EDA), diethyltriamine (DETA), triethylenetetramine (TETA), and 1,6-hexanediamine (HDA), with the proviso that (EDA) is used only in a mixture, the weight ratio of polyfunctional amine to PMPPI being in the range of 0.1:1 to 1:1, thus forming microcapsules having a polyurea shell wall around the water immiscible droplets;
- e) curing the microcapsules by continuing the agitation while heating the dispersion at a temperature in the range of 35.degree. to 60.degree. C. for a period of 3 to 10 hours to produce a formulation in which the average size of the microcapsules is in the range of 5 to 50 microns;
- f) optionally adjusting the pH to between 6.5 and 9.0.

2. A process according to claim 1 in which the emulsifier is a polyvinyl alcohol; the antifoam agent is a polydimethyl siloxane; the ratio of clomazone to PMPPI is 4.5:1 to 4.7:1; the polyamine is a mixture of TETA and HDA in which the ratio of TETA to HDA is 3:1 to 1:3; the microcapsules are cured at 45.degree. to 50.degree. C. for 4 to 5 hours and have an average size of 5 to 30 microns.

4. A process according to claim 1 in which the emulsifier is a polyvinyl alcohol; the antifoam agent is a polydimethyl siloxane; the ratio of clomazone to PMPPI is 4.5:1 to 4.7:1; the polyamine is a mixture of DETA and HDA in which the ratio of DETA to HDA is 3:1 to 1:3; the microcapsules are cured at 45.degree. to 50.degree. C. for 4 to 5 hours and have an average size of 5 to 30 microns.

6. A process according to claim 1 in which the emulsifiers are a polyvinyl alcohol and, optionally a sodium salt of sulfonated naphthalene condensate; the antifoam agent is a polydimethyl siloxane; the ratio of clomazone to PMPPI is 4.5:1 to 4.7:1; the polyamine is DETA, the microcapsules are cured at 45.degree. to 50.degree. C. for 4 to 5 hours and have an average size of 5 to 30 microns.

8. A process for the preparation of herbicidally effective formulations of clomazone having a volatility less than fifty percent of the volatility of an emusifiable concentrate of clomazone containing four pounds of clomazone per gallon of formulation which comprises microencapsulating the clomazone by interfacial polymerization by the steps of:

a) providing an aqueous phase containing 0.5 to 3.0 wt. % of one or more emulsifiers; optionally 0.05 to 0.20 wt. % of a xanthan gum viscosity modifier/stabilizer, and 0.3 to 1.0 wt. % of an antifoam agent;

b) providing a water immiscible phase consisting of clomazone, polymethylene polyphenyl isocyanate (PMPPI), and a hydrocarbon solvent; the weight ratio of clomazone to PMPPI being in the range of 1:1 to 6:1;

c) emulsifying the water immiscible phase in the aqueous phase, forming a dispersion of water immiscible droplets throughout the aqueous phase;

d) agitating the dispersion while adding thereto at least one polyfunctional amine selected from diethyltriamine (DETA), triethylene-tetramine (TETA) and 1,6-hexanediamine (HDA), the weight ratio of polyfunctional amine to PMPPI being in the range of 0.1:1 to 1:1, thus forming microcapsules having a polyurea shell wall around the water immiscible droplets;

e) curing the microcapsules by continuing the agitation while heating the dispersion at a temperature in the range of 35.degree. to 60.degree. C. for a period of 3 to 10 hours;

f) optionally adjusting the pH to between 6.5 and 9.0.

9. An herbicidal composition containing from 1 to 4 pounds of clomazone per gallon of formulation and having a volatility less than fifty percent of the volatility of an emusifiable concentrate of clomazone containing four pounds of clomazone per gallon of formulation, comprising:

a) an aqueous suspension of microcapsules made up of a polyurea shell surrounding a core of clomazone and a minor amount of a hydrocarbon solvent, the polyurea having been formed from the interfacial reaction of polymethylene polyphenyl isocyanate (PMPPI) with ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), or 1,6-hexanediamine (HDA), or a mixture of the polyfunctional amines, with the proviso that EDA is used only in a mixture;

b) 0.2 to 1.00 wt. % polyvinyl alcohol;

c) 0.1 to 0.5 wt. % antifoam agent;

d) optionally 0.07 to 0.30 wt. % xanthan gum viscosity modifier/stabilizer; and

e) 0.75 to 7.0 wt. % propylene glycol, the average size of the microcapsules being in the range of 5 to 50 microns and having a suspensibility of greater than 70%, a viscosity of 1700 to 3800 cps, and a 100 mesh wet screen analysis of greater than 99.95%.